

**Module 4.****Understanding and using logs and exponential equations****4E Multiplying with logs**

To go much further with this we need to know a little more about logs and how they work. In particular we need to know how to add, subtract, multiply and divide them.

Remember that when you multiplied two numbers in scientific notation, you added the exponents. Let's generate some rules for manipulating logs.

$$x = 10^a \quad \text{and} \quad y = 10^b \quad \text{and} \quad xy = 10^{a+b}$$

$$\log_{10}x = a \quad \text{and} \quad \log_{10}y = b \quad \text{and} \quad \log_{10}xy = a + b$$

So now the rule for multiplying logs is ...  $\log_{10}(x \times y) = \log_{10}x + \log_{10}y$

**4F Dividing with logs**

And for dividing we have...

$$x = 10^a \quad \text{and} \quad y = 10^b \quad \text{and} \quad x/y = 10^{a-b}$$

$$\log_{10}x = a \quad \text{and} \quad \log_{10}y = b \quad \text{and} \quad \log_{10}(x/y) = a - b$$

So now the rule for dividing logs is ...  $\log_{10}\left(\frac{x}{y}\right) = \log_{10}x - \log_{10}y$

**4G The log of a power of a power**

$$x = 10^a \quad x^b = (10^a)^b = 10^{ab}$$

$$\log_{10}x = a \quad \log_{10}x^b = ab \\ = ba \\ \log_{10}x^b = b\log_{10}x$$

The rule for the log of a power of a power is ...  $\log_{10}x^b = b.\log_{10}x$

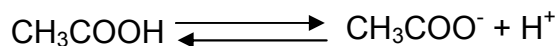


### 4H The Henderson-Hasselbalch Equation.

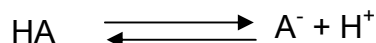
Weak acids (and most biologically relevant acids are weak acids) may be only partially dissociated in aqueous solution, therefore the pH will depend on the degree of dissociation, otherwise known as the dissociation constant or  $pK_a$ . Weak acids are useful because they can be used as buffers – that is solutions which keep the pH (fairly) constant. This is very important in physiological systems where variations in pH by even small amounts can lead to cell death.

The Henderson-Hasselbalch equation is really useful and we will see how useful later. But first I want to show use how we get to it. You will be able to follow this better if you are familiar with the rules of manipulating logarithms that we have just seen.

Acetic acid is  $CH_3COOH$  - when dissolved in water it can dissociate to give a  $H^+$  and  $CH_3COO^-$



More generically, acids can be written as HA where HA is the acid and A<sup>-</sup> is the conjugate base.



HA has a dissociation constant defined as...

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Now I know where I want to get to so I'm going to rearrange this to end up with something useful. Rearrange by dividing throughout by [H<sup>+</sup>] and K<sub>a</sub> ...

$$\frac{1}{[\text{H}^+]} = \frac{1}{K_a} \cdot \frac{[\text{A}^-]}{[\text{HA}]}$$

Taking the logs of both sides ... (remember to use the rules for manipulating logs that we have learned)

$$\log\left(\frac{1}{[\text{H}^+]}\right) = \log\left(\frac{1}{K_a}\right) + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\text{Now } \log\left(\frac{1}{[\text{H}^+]}\right) = \log([\text{H}^+]^{-1}) = -\log([\text{H}^+]) = \text{pH by definition}$$

$$\text{Similarly } \log\left(\frac{1}{K_a}\right) = -\log(K_a) \text{ is defined as } \text{p}K_a$$

So replacing  $-\log(K_a)$  with pK<sub>a</sub> and  $-\log([\text{H}^+])$  with pH ...

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

I started with the definition of K<sub>a</sub>, and just by rearranging, I've come up with something useful.

**The Henderson-Hasselbalch eqn**      $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$

*Some applications:*

(1) Something interesting happens when [A<sup>-</sup>] = [HA] – what is it?

answer: when [A<sup>-</sup>] = [HA] then  $\log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \log(1) = 0$  and  $\text{pH} = \text{p}K_a$

So if the pH is the same as the pK<sub>a</sub>, the concentration of acid and base are the same

(2) If you have added known concentrations of an acid and conjugate base (for example acetic acid and sodium acetate) and you know the  $pK_a$  (you can look it up – there are tables of all the common weak acids) then you can calculate the pH of the solution.

(3) If you know the pH (which you can measure) and the  $pK_a$  (which you can look up in a reference book), then you can calculate the ratio of  $A^-/HA$ . Why might you want to know the ratio of  $A^-/HA$ ? Think about the example of drug absorption in the stomach. The stomach is very acidic ( $pH \sim 2$ ). If your drug has a  $pK_a \sim 2$ , then roughly half of it will be present as  $A^-$  and half as HA. Now cell membranes are hydrophobic so the charged form ( $A^-$ ) will not cross into the bloodstream whereas the uncharged form will. What happens if you change the stomach pH or move into the small intestine where the pH is higher – say pH 8? Work it out with the HH eqn..

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$8 = 2 + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$6 = \log\left(\frac{[A^-]}{[HA]}\right)$$

$$10^6 = \frac{[A^-]}{[HA]} = 1,000,000$$

So the ratio of  $[A^-]$  to  $[HA]$  is 1,000,000 to 1.

$$\begin{aligned} \text{And the fraction dissociated is } & \frac{[A^-]}{[A^-] + [HA]} \times 100\% \\ & = \frac{[A^-]}{\frac{[A^-]}{[HA]} + 1} \times 100\% \\ & = \frac{1000000}{1000000 + 1} \times 100\% \\ & \sim 100\% \end{aligned}$$

So now the drug is fully dissociated and will not cross the cell membrane into the bloodstream at all.